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Author(s)	
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Division of Multidisciplinary Chemistry – Molecular Rheology –

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Prof

WATANABE, Hiroshi
(D Sc)



Assoc Prof

MATSUMIYA, Yumi
(D Eng)

Students

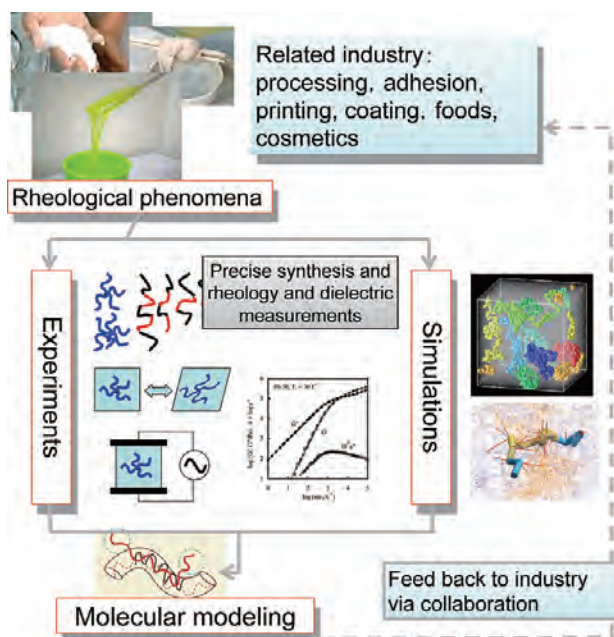
MARUYAMA, Tatsuki (UG)
MOTEKI, Wataru (UG)

Scope of Research

Research focus is placed on the molecular origin of rheological properties of various materials. Depending on time and temperature, homogeneous polymeric materials exhibit typical features of glass, rubber, and viscous fluid while heterogeneous polymeric systems exhibit plasticity in addition to these features. For basic understanding of these features, the molecular motion and structures at various scales are studied for polymeric systems in deformed state. Rheological measurements are performed with various rheometers. Auto-correlation of the molecular orientation is also investigated with dynamic dielectric spectroscopy. Analysis of rheological and dielectric behavior elucidates a new aspect of softmatter physics.

KEYWORDS

Rheology Dielectric Spectroscopy Softmatter



Selected Publications

Kwon, Y.; Matsumiya, Y.; Watanabe, H., Dielectric Relaxation of Type-A Chains Undergoing Head-to-Tail Association/Dissociation: Difference from Head-to-Head Case and Correlation with Viscoelastic Relaxation, *Macromolecules*, **52**, 8484-8502 (2019).
Morelly, S. L.; Palmese, L.; Watanabe, H.; Alvarez, N. J., Effect of Finite Extensibility on Nonlinear Extensional Rheology of Polymer Melts, *Macromolecules*, **52**, 915-922 (2019).

Dielectric Relaxation of Type-A Chains Undergoing Head-to-Tail Association/Dissociation: Difference from Head-to-Head Case and Correlation with Viscoelastic Relaxation

Dielectric relaxation of type-A chains reflects global motion of the chains but is also affected by relative alignment of the dipoles along the chain backbone, namely, by the dipole inversion. Head-to-head association of type-A unimers gives a symmetrically dipole-inverted dimer, and the association/dissociation equilibrium of these unimers and dimer results in motional coupling of these chains, thereby affecting the dielectric behavior. In fact, for this head-to-head case, eigenmode analysis has been reported in the literature to reveal that motional coupling results in moderate retardation and acceleration of the dielectric relaxation of the unimer and dimer obeying the reptation dynamics. In contrast, the coupling has no effect on the dielectric relaxation of the Rouse unimer and dimer, namely, the effect of motional coupling on the dielectric relaxation changes with the type of chain dynamics. This effect was not clarified for head-to-tail associating unimers and their dimer having no dipole inversion (Figure 1). Thus, for completeness, this study makes the eigenmode analysis of the dielectric relaxation for this case of head-to-tail reac-

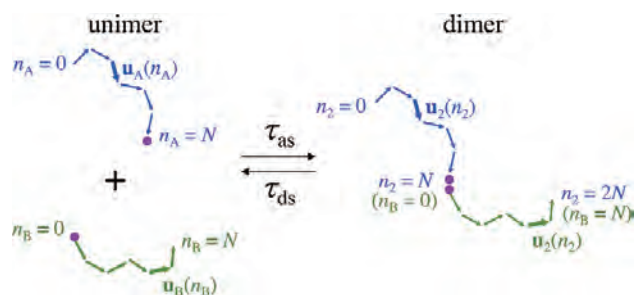


Figure 1. Illustration of head-to-tail associating unimers and dissociating dimer at equilibrium. Purple circles at N-th and 0-th segments of the blue and green unimers (A and B) indicate the associative head and tail, respectively. The unimers and dimer have type-A dipoles aligned along the chain backbone without inversion.

tion. For the unimer and dimer obeying either Rouse or reptation dynamics, the analysis indicates that the retardation and acceleration of the dielectric relaxation of the unimer and dimer are much more significant for the head-to-tail case than for the head-to-head case irrespective of the chain dynamics, and that the dielectric relaxation function for the former case exactly coincides with the viscoelastic relaxation function if the unimer and dimer obey the reptation dynamics (Figure 2). This result suggests an interesting method of resolving some detail of the chain dynamics under the reaction through comparison of dielectric and viscoelastic responses of the associative type-A chains.

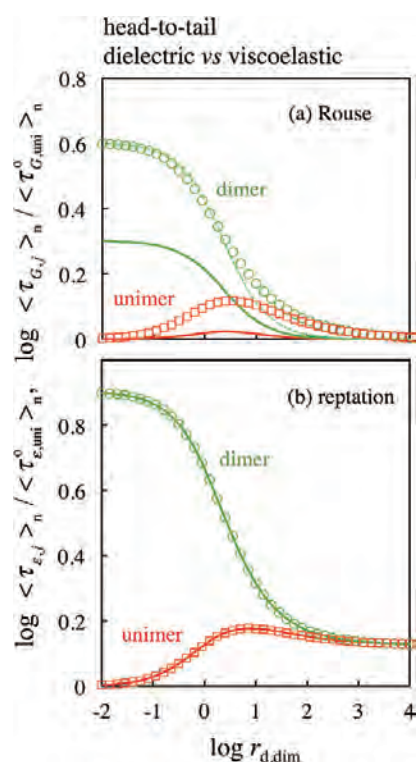


Figure 2. Terminal viscoelastic and dielectric relaxation times, $\langle \tau_{G,j} \rangle_n / \langle \tau_{G,uni}^0 \rangle_n$ and $\langle \tau_{e,j} \rangle_n / \langle \tau_{e,uni}^0 \rangle_n$ (solid curves and symbols), of the unimer and dimer undergoing head-to-tail reaction plotted against normalized dissociation rate $r_{d,dim}$ (set identical to $r_{a,dim}$). For comparison, $\{ \langle \tau_{G,2} \rangle_n / \langle \tau_{G,uni}^0 \rangle_n \}^2$ for the Rouse dimer is shown with the dashed green curve in the top panel.